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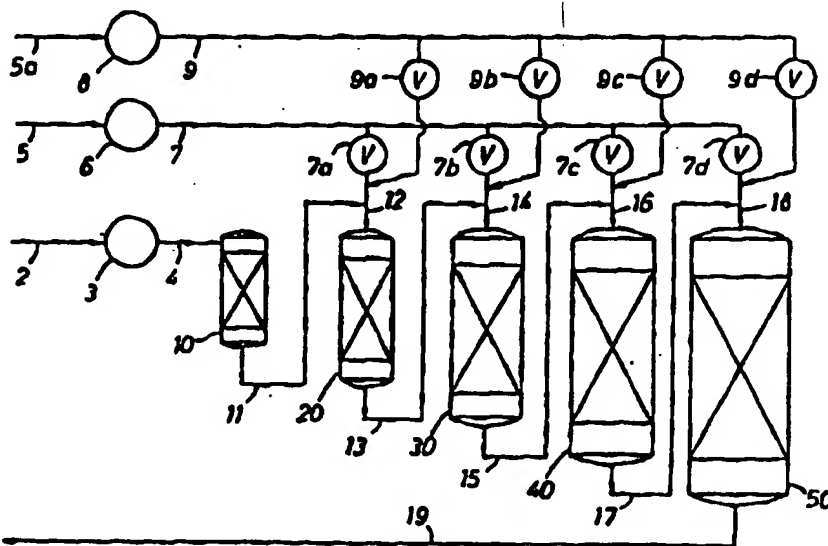
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08/625,365 1 April 1996 (01.04.96) US(71) Applicant: STARCHEM TECHNOLOGIES, INC. [US/US];  
10822 Fawnview, Houston, TX 77070 (US).(72) Inventor: VAN DIJK, Christian, P.; 10722 Glenway, Houston,  
TX 77070 (US).(74) Agent: COX, Charles, M.; Pravel, Hewitt, Kimball & Krieger,  
10th floor, 1177 West Loop South, Houston, TX 77027-  
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(54) Title: FIXED BED CONVERSION OF METHOXY COMPOUNDS TO OLEFINS



## (57) Abstract

This invention relates to a process for converting alkoxy compounds over a fixed bed of catalyst into olefinic compounds, mostly ethylene and propylene. This process proceeds with low heat exchange duty requirements for heating the alkoxy compounds and recycle streams used as feedstocks and for final cooling of reaction product gases for recovery of olefin product while at the same time offering an improved choice of operating conditions. As may be desired, steam may be added to obtain a desired final steam partial pressure in all catalyst contacts with the alkoxy compounds.

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### FIXED BED CONVERSION OF METHOXY COMPOUNDS TO OLEFINS

This invention relates to a process for converting alkoxy compounds into hydrocarbons which are olefins, mostly as ethylene followed by propylene.

Catalysts for the conversion of alkoxy compounds, such as methanol and/or dimethyl ether, to gasoline grade saturated hydrocarbons with some aromatics are known, as disclosed by various Mobil Oil Corporation patents issued beginning in the 1970's. In an article by C. D. Chang and A. J. Silvestri in the October 1987 issue of Chem Tech about the conversion of methanol to gasoline (MTG), it was mentioned that appreciable amounts of olefins (i.e., unsaturated hydrocarbons) can be generated by the same catalyst when the conditions of the conversion are modified. At a low pressure (0.04 ata) the C<sub>2</sub> to C<sub>5</sub> olefins were reported to be as much as about 80% of the hydrocarbon products of reaction.

Since the advent of a catalyst for the conversion of methanol to gasoline, worldwide only one commercial installation which practices the methanol to gasoline ("MTG") process has been constructed. That installation is in New Zealand. Conceived in the late 1970's when crude oil prices were expected to reach a \$40/barrel range the installation then appeared to be economically feasible. The New Zealand MTG facility is basically a natural gas to methanol (GTM) plant (as the front end) coupled to a methanol to gasoline (MTG) plant operating with an MTG catalyst in a plurality of fixed catalytic bed reactors arranged in parallel, each for single pass methoxy feed gas flow. The arrangement comprises five MTG reaction vessels, four of which operate at any given time while one is off stream during which MTG catalyst may be regenerated or replaced as desired.

Between the conception of the New Zealand fixed bed GTM-MTG facility with its attendant high capital and operational cost commitments and the time that facility was completed and ready for on-stream operations (at a capital cost obligation of about \$1.2 billion) the worldwide price of crude oil drastically declined to its current day levels of about \$20/barrel. At today's cost of crude oil, gasoline produced from methanol by a fixed bed process as followed in the New Zealand facility is competitively uneconomical in comparison to gasoline refined from crude oil. In one respect the New Zealand GTM approach is too costly in the conversion of natural gas into methanol. The present inventor, together with Lowell D. Fraley, has described a natural gas to methanol conversion process with much lower expected capital costs in U.S. Patent Nos. 5,177,114 and 5,245,110. Yet, even with this lower cost for methanol the New Zealand process of fixed bed conversion of methanol to gasoline (MTG) would still be too high in capital cost.

A major reason that the methanol to gasoline part of the New Zealand facility is uneconomical is because of the heat exchange duties -- both in capital and perational cost -- required for proper operation of a methanol to gasoline catalyst (MTG catalyst) in a fixed bed reactor. For proper operation of an MTG catalyst in terms of its activity and aging, it must  
5 be exposed to a particularly controlled environment of temperature and water concentration while it is in contact with the methanol (or other methoxy compounds) that it converts to gasoline grade saturated and aromatic hydrocarbons. If exposed to too low of a temperature, an MTG catalyst will not be active or will be of such low catalytic activity to be of no interest. Exposed to too high of a temperature, the MTG catalyst will so prematurely "age" and/or be destroyed so as to  
10 be economically impractical for use.

This problem of the temperature sensitivity of an MTG catalyst is compounded by the problem of its need for the presence of water in order for it to be catalytically active. Too little water in its presence and it is inactive or of such low activity to be of little practical interest. Depending upon its temperature exposure, too high a concentration of water and the MTG  
15 catalyst ages so prematurely and/or is destroyed so as to render its economical use unfeasible.

These temperature/water sensitivity problems attendant to use a MTG catalyst are further complicated by the fact that the reaction of methanol (or other methoxy compounds) to gasoline which it catalyzes is fast and highly exothermic, thus causing a high degree of heat release (i.e., heat of reaction) at the reaction site. If not moderated by some means, methanol and/or dimethyl  
20 ether fed into contact with a fixed bed of MTG catalyst at an inlet temperature of 710°F would react to form a product gas having a temperature greater than 2,000°F. Such a temperature rise within an MTG reaction vessel is not tolerable. The temperature rise caused by heat released by the MTG reaction in a fixed bed of catalyst cannot be controlled within acceptable product gas exit temperature limits -- i.e., 730°F to 800°F -- by direct heat exchange methods because the  
25 MTG reaction is too fast.

The need of an MTG catalyst for a sufficient, though limited, exposure to water coupled with its need for exposure to a sufficient, though limited, range of temperature to be sufficiently active, coupled to the fact that it catalyzes a fast and highly exothermic reaction, have entailed a number of processing complexities associated to the heat exchange requirements attendant to  
30 the proper operation of a methanol to gasoline process with a fixed bed MTG catalyst.

In order to accommodate the temperature range exposure requirements of MTG catalyst, the New Zealand facility effectuates product gas temperature control within the MTG fixed bed catalyst vessels by recycle through the reactor as a temperature diluent the C<sub>2</sub> and C<sub>3</sub>.

hydrocarbon by-product gases remaining after the reactor product gases are cooled down from their reaction temperature of about 800°F to about 100°F for removal of their gasoline grade liquid hydrocarbon product and water content. In order to limit the temperature rise in the fixed bed MTG reactor to less than about 100°F, this recycle diluent gas is added in an amount  
5 compared to the methoxy feed gas (methanol, dimethyl ether, etc.) of about 12.4 moles diluent recycle gas/mole methoxy equivalent. For every 1 volume of methoxy equivalent with which it is combined to form the feedstock gas for the MTG reaction it is therefor necessary to heat about 12.4 volumes of the C<sub>2</sub> and/or C<sub>3</sub>, recycled diluent gas from its recovery temperature of about 100°F to the minimum temperature required by an MTG catalyst for sufficient activity, which  
10 is a reactor inlet temperature of about 650°F and preferably about 700°F. This imposes a tremendous heat exchange burden both in terms of reactor effluent gas cool down (800°F to 100°F) for gasoline grade hydrocarbon product recovery and recycle gas (C<sub>2</sub>/C<sub>3</sub>,) reheat (from 100°F to at least 650°F, and preferably to 700°F) for use as diluent gas for fresh methoxy feed to the MTG reactor. For each gas volume of hydrocarbon product produced about 71 volumes  
15 of recycle diluent gas must be heated up by about 600°F and later cooled down by about 700°F in adiabatic heat exchanger units.

In the New Zealand MTG operation the feedstock methoxy compound, generally in the form of an equilibrium gas mixture of methanol, dimethyl ether and water vapor, is combined with a recycle gas comprising C<sub>2</sub> and C<sub>3</sub>, hydrocarbons then heated to the reactor inlet  
20 temperature of about 700°F. Thereafter, the methoxy content of this feed gas is reacted in a single pass over a fixed bed MTG catalyst to produce a product gas of about 800°F with a partial pressure of water (as steam) of about 2 atmospheres absolute (ata) at a product gas pressure of about 22.3 ata. Hence, heat exchange operations to heat up feed gases and/or cool down product gas are carried out on gas streams at a pressure of about 22.3 ata.

25 The MTG reaction gases are cooled from their reaction temperature, T<sub>R</sub>, to their final cool-down temperature, T<sub>O</sub>, in two heat exchange operations. In the first operation the reaction gases are indirectly heat exchanged with fresh feedstock gases through adiabatic heat exchangers to cause the feedstock gases to warm up from their unit available temperature of about T<sub>O</sub> to their reactor inlet temperature T<sub>I</sub> by transferring thereto of a quantity of heat Q from the reaction gases  
30 which thus causes the reaction gases to cool down from their reaction temperature T<sub>R</sub> to their first cool down temperature T<sub>X</sub>. Thereafter, the reaction gases are finally cooled from their first cool down temperature T<sub>X</sub> to the liquid hydrocarbon recovery temperature, T<sub>O</sub>, either by direct or indirect heat exchange contact with chill water.

For purposes of simplifying a discussion of the heat exchange burden associated to operation of the New Zealand fixed bed MTG process, one may assume that the specific heat content of a fresh feedstock gas about equals the specific heat content of the reaction product gas which results from this feed gas. Under this circumstance, when the reaction product gas gives up a quantity of heat  $Q$  to heat up a new portion of feed gas from  $T_O$  to  $T_I$  the reaction gas cools to a temperature  $T_X = T_R - (T_I - T_O)$ . To finally cool the reaction gas to a temperature  $T_O$  to recover its liquid hydrocarbon and water content the quantity of heat that must further be removed from the reaction product gas equals the heat of condensation and that quantity of heat resulting from the heat of the MTG reaction of the methoxy compound from which the reaction gas was formed.

Generally, in the New Zealand situation, the adiabatic heat exchangers through which feed gas is heated up while the MTG reaction product gas is cooled down are on the order of 3-4 times as expensive as those heat exchange units by which the product gas is finally cooled down to condense the normally liquid hydrocarbon content by heat exchange with chill water. Further, the sizing of these adiabatic heat exchange units, which bears very significantly on their cost, is directly effected by the difference in temperature to which the fresh feedstock gases are to be heated and the temperature from which the product gases are to be cooled ( $\Delta T$ ) and the pressure ( $P$ ) of the gases to be heated and cooled. The larger the differential temperature ( $\Delta T$ ) and/or the higher the pressure ( $P$ ) the more efficient is the heat exchange process and the smaller can be the size of the heat exchanger needed. The relative heat exchange surface area ( $A_R$ ) required to transfer this quantity of heat ( $Q$ ) is generally given by the formula  $A_R = Q (1/\Delta T)(1/P)^{0.6}$ .

Here, with respect to a fixed bed operation with an MTG catalyst wherein feedstock methoxy-recycle diluent gas is brought from a temperature of 100°F to an reactor inlet temperature of 700°F and reacts over the MTG catalyst to produce a product gas of 800°F at a pressure such that the partial pressure of steam in the product gas is 2 ata, for a methanol feed containing 100 lb-moles of MeOH and 11.84 wt%  $H_2O$  (or 23.87 lb-moles  $H_2O$ ) that is preconverted to an equilibrium mixture of DME and MeOH (23.18 MeOH, 38.41 DME, 62.276  $H_2O$ ) which is then used in the feedstock, about 1240 lb-moles of diluent  $C_2-C_3$ , recycle gas must be added to moderate the heat of the MTG reaction to the temperature rise from the 700°F inlet to an 800°F outlet temperature (the MTG heat of reaction of MeOH = 24,000 BTU/lb-mole and of DME - 35,200 BTU/lb-mole). Defining the heat content of a material at 0°F to be zero, then under these conditions at a final pressure of 22.3 ata of the product gas its steam partial pressure will be 2 ata and the 800°F product gas will have a heat content of 15,266,384 BTU. Use of this

product gas as the hot fluid for an adiabatic heat exchanger to heat up a new charge of feedstock from 100°F (and having a heat content of 1,908,298 BTU) to 700°F (wherein it would have a heat content of 13,358,086 BTU) requires a transfer of 11,449,788 BTU from the hot product gas to the cooler feedstock gas while both gas streams are at a pressure of about 22.3 ata. The relative  
5 heat exchange surface area ( $A_R$ ) required to accomplish this is therefore:

$$A_R = 11,449,788 (1/100)(1/22.3)^{0.6} = 17,775$$

This then may be referred to as a point of reference for comparing the expense of heat exchange operations when one desires to compare other operational methods to that of a fixed bed MTG process as practiced by the New Zealand installation.

10 The temperature rise/water concentration dilemma that hampers the MTG conversion process over a fixed bed of MTG catalyst as being an economically competitive process for gasoline production compared to that of gasoline refined from natural crude oil remains unsolved by any prior art suggestion.

As before mentioned, in the mid 1980s it was noted that under certain conditions a  
15 significant quantity of olefins--particularly ethylene and propylene--may be produced by contact of a methoxy compound with an MTG catalyst. As the value of such olefins is substantially greater than that of gasoline grade hydrocarbons, since the time of that observation consideration has been given to the commercial feasibility of converting methanol to olefins ("MTO"). A catalyst compositions of greater selectivity for MTO conversion have since been developed, as  
20 described in such presentation papers as those by Jeffrey M.O. Lewis et al, "Methanol to Olefins Process Using Silicoaluminophosphate Catalyst," Copyright 1988 Union Carbide Corporation; B.V. Vora et al., "Gas To Olefins Using The New UOP/Hydro MTO Process," presented to Gas Processors Association GCC Chapter in Bahrain on November 22, 1995; and B.V. Vora et al., "Economic Route For Natural Gas Conversion To Ethylene and Propylene," presented to 4th  
25 International Natural Gas Conversion symposium held at Kruger National Park, South Africa on November 19-23, 1995.

As described by these presentation papers, an improved catalyst composition for the MTO reaction, SAPO-34, was initially verified in micro-reactors using unbound crystals--i.e., in a one inch fixed bed reaction with a powdered form of catalyst. Nevertheless, the potential significant  
30 conveniences of a fixed bed reactor were discarded and a fluidized bed with continuous catalyst regeneration process was instead proposed and evaluated for the commercial feasibility of implementing an MTO process. Apart from the high coke make experienced when switching from catalyst in the form of unbound crystals to a formulated catalyst, the advocacy of a

fluidized bed reactor for practice of an MTO process was no doubt influenced by the previous experience with the heat exchange duties attendant to practice of an MTG process in fixed beds as in the New Zealand installation, as previously discussed, together with the fact that the MTO reaction is highly exothermic and also requires means for moderating the temperature rise across the catalyst in an MTO reaction zone.

Because the heat of reaction of methoxy conversion to olefins is significantly less and therefore less recycle gas diluent is required for temperature rise moderation than that for methoxy conversion to gasoline grade hydrocarbons, in order to maintain a partial pressure of water (as steam) over the MTO catalyst in a range most efficient for best catalyst performance (i.e., water partial pressure of about 1.5 to 3.0 ata) the total pressure at which an MTO reaction may be conducted is significantly lower than the total pressure at which an MTG reaction is conducted. Since operations of an adiabatic heat exchanger are less efficient with lower gas pressures than at higher gas pressures, the lesser heat content of of a MTO reaction gas would ultimately be removed by a heat exchanger operating at a lower efficiency.

For instance, to operate with a fixed bed of MTO catalyst under the same conditions of feed inlet temperature (700°F), product gas outlet temperature (800°F); and partial pressure of steam (2 ata), using adiabatic heat exchangers to warm up feed gas from 100°F to 700°F by heat exchange with hot product gas at 800°F, since the MTO heat of reaction of MeOH = 10,596.7 BTU/lb-mole and DME = 8,393.4 BTU/lb-mole, a lesser amount of temperature moderating recycle gas must be added in the feed, namely to a methoxy charge of 23.18 MeOH, 38.41 DME and 62.276 H<sub>2</sub>O there is added 204.12 lb-moles of dry olefin product gas (specific heat 18.5 BTU/°F/lb-mole) as diluent recycle. Again, defining the heat content of a material at 0°F to be zero, this methoxy-recycle feedstock gas as formed at 100°F has a heat content of 568,022 BTU and after preheating to the 700°F inlet temperature has a heat content of 3,976,154 BTU. Upon contact with an MTO catalyst the methoxy content of this feed gas reacts to olefins with a release of 568,022 BTU of heat to form a product gas of 800°F comprising 120.87 H<sub>2</sub>O, 204.12 recycle diluent and 44 olefin product having a heat content of 4,544,176 BTU and at a pressure of 6.1 ata a partial pressure of steam (H<sub>2</sub>O) of 2 ata. Use of this hot 800°F product gas as hot fluid in an adiabatic heat exchanger to warm up a methoxy-recycle feedstock from 100°F to 700°F requires a heat transfer of 3,408,132 BTU between gases at about 6.1ata. The relative heat exchange surface area (A<sub>r</sub>) required would be:

$$A_r = 3,408,132 (1/100)(1/6.1)^{0.6} = 11,516$$

This, by comparison to an MTG fixed bed process, is a lesser heat exchange burden but is still



unacceptable in terms of the capital and operational cost of the heat exchange duty required.

Hence, practice of an MTO process in a fixed bed arrangement similar to that in which an MTG process is actually practiced in New Zealand would be expected to require a comparable heat exchanger duty -- i.e., one that is intensively costly both in its capital and operational requirements.

In a fluid bed method of MTO operation as instead advocated, as reported a significant quantity of the methoxy feed is lost to coke production (3% of feed carbon) that builds up on the catalyst particles - hence requires continuous catalyst regeneration while also lowering the yield of desired olefin product as a per cent yield on carbon. This would appear to be burden inherent in operation by a fluidized bed process since in a fixed bed practice of a MTG process as done in New Zealand coke buildup on a fixed bed catalyst appears to proceed at a negligible rate by comparison - catalyst regeneration being needed only on infrequent periodic basis after months of operation. Further, the coke producing reaction which occurs in a fluidized bed operation also seems to be associated to a greater production of saturated hydrocarbon and other by-products, further reducing olefin yield.

If not for the huge heat exchanger cost associated to the fixed bed mode of operation with an MTG catalyst -- or by analogy, with a fixed bed of MTO catalyst -- a fixed bed operation would be preferred for its greater simplicity of reactor cost and operation and for its reduced formation of coke by-product and possible reduction of other nonolefinic by-products.

In accordance with the process described by this invention, it is possible to substantially reduce the heat exchange duties entailed in the proper operation for activity and aging regulation of an MTO catalyst in a fixed bed mode while also properly controlling the exposure of such catalyst to a water concentration. It is expected that a fixed bed operation will result in significantly higher yields of ethylene and propylene and also result in improved ethylene to propylene ratios.

To significantly reduce the heat exchange requirements for proper temperature control of the reaction of an alkoxy compound over a fixed bed of MTO catalyst, and at the same time control the steam partial pressure in the process within narrow limits, aiming thus to have the MTO reaction proceed under proper temperature and steam pressure control without at any time endangering the MTO catalyst, the invention proposes a method for operation of an MTO process wherein:

(1) Successive reaction zones containing a fixed bed of MTO catalyst are employed wherein a product effluent gas of temperature  $T_{r_p}$  from a preceding MTO reaction ( $r_p$ ) is

combined with a new charge of feed gas comprising an alkoxy compound and a diluent gas which may comprise a portion of the hydrocarbon products of the MTO reaction, steam, or mixtures thereof. This new charge of feed gas is preheated to a temperature  $T_p$  that is less than  $T_r$  and mixed with the preceding product effluent gas to form a combined gas mixture that is of a desired temperature  $T_i$  and specific heat content to be contacted with a fixed bed of MTO catalyst in a succeeding reaction zone ( $r_i$ ) to convert its alkoxy compound content to olefinic hydrocarbon products contained in a new product gas stream having a temperature  $T_{r_s}$ . In warming up the new alkoxy-recycle feed gas charge from its preheat temperature  $T_p$  by mixing it with the earlier hot effluent product gas at  $T_p$  to obtain as a result a combined gas mixture of temperature  $T_i$ , the warmup is obtained without heat exchangers, which otherwise would have been necessary to warm the new feed gas up to the desired  $T_i$  reactor inlet temperature; further the lower diluent recycle content of the fresh feed gas would not allow entry of that feed as such at the desired reactor inlet temperature without its reaction to a temperature greater than the  $T_{r_s}$  temperature desired for the outlet from the reactor.

(2) The new charge of alkoxy compound provides an alkoxy equivalent value which exceeds that which was added to the preceding MTO reaction zone and the new charge of diluent gas provides the combined gas stream with a specific heat content that upon reaction of the new charge of alkoxy compound to olefinic hydrocarbon compounds limits the temperature rise ( $\Delta T_R$ ) within the succeeding MTO reaction zone to less than 150°F, preferably less than 100°F and most preferably less than 75°F.

(3) The new charge of alkoxy compound and diluent gas are preheated before combination with the product effluent gas to a temperature  $T_p$  that is below the desired reactor inlet temperature  $T_i$ , so that on taking an appropriate amount of this new charge for addition to the effluent gas from the preceding reactor a mix temperature of  $T_i$  will be obtained for the combined gas mixture, whereafter contacting the combined gas mixture with a sufficient amount of MTO catalyst the succeeding reaction will produce a new effluent gas temperature of  $T_R$  which is at a desired level. As desired, each MTO reactor in the series may be operated with the same  $T_i$  and  $T_R$  temperatures or any reactor within the series may be operated at a  $T_i$  and  $T_R$  temperature selected for it which is different than that of other reactors in the series, this being accomplished by the proper choice of the alkoxy and recycle content of the new feed gas charge to be added to the succeeding reactor and the quantity of this new feed charge to be combined with the product effluent gas from the preceding reaction.

(4) As desired, a portion of the new charge of diluent gas may comprise water in an

amount that together with the water carried over with the product effluent gas and the water formed by reaction of the new charge of alkoxy compound provides a total water content in the new product effluent gas that at the outlet pressure of the succeeding MOT reaction zone provides for any partial pressure of water desired, such partial pressure of steam (water) preferably will be in the zone of 0.5 to 3.0 ata, preferably 1.5 to 2.8 ata, most preferably in the zone between 1.8 and 2.4 ata.

According to this invention the total amount of alkoxy equivalent processed to olefinic products is proportioned among a plurality of MTO reaction zones and the alkoxy equivalent quantity provided to each MTO reaction zone generally increases in progression from the first to the last or final MTO reaction zone. This method of operation provides for great flexibility in the operational conditions of temperature and pressure at which a given MTO reaction zone may be operated relative to another in order to achieve a variety of desirable objectives, all attendant with a significant reduction in the heat exchange duties otherwise required to process the same total amount of methoxy equivalent to olefinic products by a single fixed bed mode of operation with the MTO catalyst.

For instance, where the activity of the MTO catalyst is the same in each zone, for uniformity of product distribution of hydrocarbon product produced in each MTO reaction zone, each desirably is operated at approximately the same pressure, the same inlet and outlet temperatures (i.e., each zone has the same  $\Delta T_R$ ), and each reaction zone, at least after the first, has about the same partial pressure of steam at the outlet of the reaction zone. Such is possible with the method of the invention. However, if because of aging or other reasons the activity of an MTO catalyst in one of the multiple zones is significantly less than another, it may be desired to operate this particular MTO reaction zone at a higher outlet partial pressure of steam ( $H_2O$ ) than the other, or at a higher  $T_R$ , this in order to enhance the activity of the MTO catalyst therein or to alter the partition of product between ethylene ( $C_2$ ) and propylene ( $C_3$ ). This too is possible with this invention.

A combination of factors leads to a significant reduction in the heat exchange duties required by the process of this invention in comparison to prior MTO and MTG fixed bed processes contemplated or employed. First, on the basis of the total methoxy equivalent ("MeO eq.") processed, with the process of this invention the diluent gas/MeO eq. mole ratio is reduced which in turn reduces the quantity of diluent gas that through adiabatic heat exchange units must be preheated for reaction temperature moderation use or, ultimately, cooled down for recovery of hydrocarbon product. This reduces the size of the heat exchangers required for feedstream

heatup and/or final product cool-down. Further, a significant quantity of the total methoxy equivalent processed, together with the recycle diluent gas needed to moderate temperature rise due to its heat of reaction, needs to be preheated to a temperature ( $T_p$ ) which is lower than the temperature ( $T_i$ ) at which it is desired to contact the methoxy compound with a fixed bed of MTO catalyst. This is achieved by admixing the methoxy-recycle feed at with hot product gases from a preceding MTO reaction (at  $T_R$ ) which heats up the added methoxy-recycle feed at  $T_p$  to the desired reaction inlet temperature  $T_R$ , while cooling down the hot reaction gases to the desired reaction inlet temperature. In this respect this aspect of the feed gas heatup/product gas cool down is performed by direct gas-gas contact, thus eliminating this portion of need for adiabatic heat exchange equipment. Also, with respect to the warmup of feedstock gases to  $T_p$  by heat exchange with reaction gases at  $T_R$  through an adiabatic heat exchanger, this also increases the heat exchanger differential temperature ( $\Delta T$ ) making the heat exchange process more efficient, meaning the heat exchanger need will be smaller.

As explained hereafter in greater detail, operations in accordance with this invention permit a selection of conditions in terms of (a) the nature of the methoxy feed, (b) the nature of the diluent gas composition, and (c) the temperature to which the feed gases are preheated before being mixed with reaction gases from a preceding MTO reaction; such that the MTO conversion can be achieved in a fixed bed of MTO catalyst with the maximum of economy in terms of the capital and/or operational cost associated therewith.

Figure 1 is a schematic illustration of a five reactor series with interstage feed of charges of alkoxy-recycle feedstock gases between the reactors in accordance with the present invention.

Figure 2 is a schematic illustration of an alternative embodiment of the process wherein a MTO reactor, which may be the first of a series of MTO reactors, recycles a portion of its product gas back to the inlet of this MTO reactor to provide a gas-to-gas exchange of heat with fresh alkoxy feed to this reactor to achieve a final warmup of the fresh feed from its  $T_p$  temperature to the  $T_i$  temperature desired for contact with the MTO catalyst therein.

The practice of this invention requires an alkoxy feedstock, generally a MeOH and/or DME feedstock, various fixed bed reaction vessels containing an MTO catalyst composition and devices for controlling the rate of feed of DME and/or MeOH,  $H_2O$  (as steam), and gas product as diluent recycle gaseous feedstock admixture components of the total feedstocks to an MTO catalyst containing reaction vessel.

The MeOH (methanol) may be formed from a coal or natural gas starting material by any of the methods well known to those skilled in art. Preferably when produced from natural gas

the methanol is produced by methods as described in U.S. Patent Nos. 5,117,144 and 5,245,110. Prior to the MTO reaction, and preferably so, the MeOH may be subject to contact with a dehydration catalyst, as is well known in the art, to convert it to an equilibrium mixture of MeOH, DME (dimethyl ether) and H<sub>2</sub>O and this gaseous mixture of methoxy components used  
5 as a preferred alkoxy feed component for an MTO catalyst contact for conversion to an olefinic product with production of by-product water. Most preferred is the use of DME alone as the alkoxy feed component. DME can easily be isolated from the equilibrium mixture and the methanol-water separately recovered can be concentrated as to its methanol content and recycled back to contact with the dehydration catalyst to make more DME containing equilibrium mixture.

10 In order to minimize the heat exchange duty requirements while regulating the temperature, pressure and water concentration conditions for the proper activity and aging regulation of an MTO catalyst during the conversion of alkoxy compounds to olefinic products, the process of this invention utilizes a plurality of MTO fixed bed catalyst zones or reaction  
15 vessels in series flow whereby the product effluent gas from a preceding MTO zone or reactor is combined with a fresh charge of alkoxy compound together with a recycle diluent gas and/or water (stream) to form a combined gas stream of a temperature and specific heat content suitable as an alkoxy-containing feed gas to a succeeding MTO zone or reactor wherein its alkoxy compound content is reacted in contact with a fixed bed of MTO catalyst to olefinic compounds. Generally, the alkoxy equivalent of the alkoxy compound added to the product effluent gas of a  
20 preceding MTO reaction exceeds the alkoxy equivalent content of the feed gas stream to the preceding reactor from which the product effluent gas was produced.

Any number of MTO reaction zones or reactors may be utilized, though generally no further particular advantage is realized in excess of ten, and more preferably five to eight MTO reaction zones or reactors in series. The product effluent gas from the final MTG reaction of the  
25 series is cooled from its final reaction temperature to about 100°F to recover its water content separate from its C<sub>2</sub> and C<sub>3</sub> gaseous hydrocarbon content. At least a portion of the dewatered gaseous hydrocarbon product is recycled for use as a temperature moderating diluent gas for combination with fresh charges of alkoxy compound and the other portion of recovered olefinic product is further refined into its various boiling point fractions, particularly ethylene and  
30 propylene.

The combination of a fresh charge of alkoxy compound and recycle dewatered product gas with the product effluent gas from a preceding MTO reaction to form a combined gas of

suitable inlet temperature ( $T_I$ ) and specific heat content as feed to a succeeding MTO reaction reduces the overall heat exchange duties with respect to the total make of olefinic product by reducing the size of the heat exchangers needed for heating the fresh charge of alkoxy compound and recycle gas to the temperature needed for admission to the succeeding MTO reactor wherein the mixture, in line with its alkoxy content and its total specific heat content, will react in contact with an MTO catalyst from temperature  $T_I$  to the desired temperature  $T_R$  for the new reactor.

For simplicity sake, assume for the moment that the specific heat value of a compound remains constant over a temperature range of 100 to 800°F (actually, the value of specific heat of a compound varies somewhat with temperature). Now take for example, conversion of 100 lb-mole per hour (MPH) of methanol (MeOH) to olefins creates a heat of reaction ( $Q_R$ ) of 100 x 10,596.7 BTU/lb-mole MeOH = 1,059,670 BTU. To limit the temperature rise of the reaction gases to  $\Delta T_R = 75^\circ\text{F}$ , for a feed gas inlet temperature  $T_I = 710^\circ\text{F}$  and an effluent gas outlet temperature  $T_R = 785^\circ\text{F}$ , the total specific heat content of the feed gas must be  $1,059,670/75 = 14,129 \text{ BTU}/^\circ\text{F}$ . Were recycle diluent gas combined with this methanol in an amount to provide a total feed gas of this specific heat content, then to preheat this total feed gas from its unit available temperature  $T_O$  of, say,  $100^\circ\text{F}$ , to the reactor inlet temperature  $T_I$  of  $710^\circ\text{F}$  would require the addition of heat to such feed gas that is  $(710-100) \times (14,129) = 8,618,690 \text{ BTU}$ . On the other hand were a quantity of recycle diluent gas added to this methanol that would allow it to increase in temperature by  $150^\circ\text{F}$  due to the reaction of methanol to olefins, the feed gas would have a total specific heat content of  $1,059,670/150 = 7,064.5 \text{ BTU}/^\circ\text{F}$ . Now the warmup of the 100 lb-mole of methanol would take away also 1,430 BRU/ $^\circ\text{F}$ , leaving 5,634.5 BTU/ $^\circ\text{F}$  to be taken away by recycle and by any water present. This translates to substantially less recycle diluent gas added. This leaner recycle feed gas, if reacted by itself, would then react from a temperature of  $635^\circ\text{F}$  to a product gas of  $785^\circ\text{F}$ . To preheat this recycle-leaner feed gas stream from  $100^\circ\text{F}$  to  $635^\circ\text{F}$  would require the addition of heat of  $(635-100) \times 7,064.5 = 3,799,507.5 \text{ BTU}$ . In accordance with this invention, by mixing this  $635^\circ\text{F}$  temperature gas having a specific heat content of  $7,064.5 \text{ BTU}/^\circ\text{F}$  with a gas stream having a temperature of  $785^\circ\text{F}$  and a specific heat content of  $7,064.5 \text{ BTU}/^\circ\text{F}$  a combined gas stream is formed having a temperature of  $710^\circ\text{F}$  and a total specific heat content of  $14,129 \text{ BTU}/^\circ\text{F}$ . Thereafter, reaction of the methanol content of this combined gas stream to olefins will increase the temperature of the gas by  $1,059,670/14,129 = 75^\circ\text{F}$  to provide an effluent gas stream having an outlet temperature  $T_R$  of  $785^\circ\text{F}$ .

As seen from the above, the quantity of heat exchange required for warmup of the leaner

recycle feed gas is significantly reduced because the quantity of recycle diluent gas is reduced, but the methanol is still converted to olefins in the same temperature zone, i.e., 710-785°F. Further, the efficiency with which the feed gas warm-up heat exchange is accomplished is significantly enhanced by reason of the increase in the differential temperature ( $\Delta T$ ) at which the heat exchangers performing this duty operate. On one hand, the rich recycle feed gas 710°F warm-up situation would require a relative heat exchanger surface area ( $A_R$ ) of  $A_{R710} = 8,618,690 (1/75)(1/P_{710})^{0.6}$  and the leaner recycle feed gas 635°F warm-up situation would require  $A_{R635} = 3,779,507.5(1/150)(1/P_{635})^{0.6}$ . The savings in heat exchange duties to be realized through the change in the differential temperature of heat exchange operations would only be offset if the difference in the pressure ( $P$ ) of the two operations were such that for the 635°F warm-up situation the pressure for operation was less than one-twelfth (1/12) that for operation of the 710°F warm-up situation. However, the change in the recycle gas amounts between the two situations does not require such drastic reduction in the pressure of the MTO operation in order to maintain the same partial pressure of steam in the resulting product gases. Instead, the pressure of operation is only reduced in roughly the same proportion as is the quantity of recycle diluent reduced. Here, in the 710°F versus the 635°F feed gas preheat situation only half the quantity of recycle is used in the 635°F feed gas, and to maintain a partial pressure of steam of 2 ata in the product gas, the pressure of the MTO operation with the 635°F feed gas is about one-half that for operation with the 710°F gas.

In those embodiments of the process of this invention wherein the first MTO reactor of the series operates on a feed gas composition that is preheated through adiabatic heat exchangers to the  $T_1$  temperature desired for its contact with the MTO catalyst therein, the heat exchange duty that this reactor contributes to the total heat exchange duty required of the overall process is significantly greater in comparison to the quantity of methoxy equivalent converted in this first reactor than is that contributed to the total of methoxy equivalent converted by the subsequent MTO reactors of the series. Hence, by using a larger number of reactor steps, the influence on the total of heat exchange duties required due to the warmup for the first reactor is greatly reduced so that the benefit of the reduction in heat exchange for the subsequently added feed gas material is then the gain for this reaction choice. For the number of reactors utilized, together with the conditions chosen for their operation, it is preferably such that no more than 20% of all alkoxy compound converted by the process is converted in the first reactor of the series, preferably no more than 10%. As made clear in the examples, the reduction of the total heat exchange duties in comparison to that for a single reaction stage processing of the same total

quantity of methoxy equivalent is substantial and can be a reduction as much as an order of magnitude.

The heat exchange burden reduction is further facilitated by using an alkoxy feed which will make a lower steam fraction and can therefore be used at higher pressure, which enhances the heat exchange efficiency. Such feeds may be obtained by removing water from the alkoxy feed. Removing water from methanol is possible by distillation but distilling raw methanol (i.e. about 14-17 wt%  $H_2O$ ) to a significantly lower water content is a rather difficult operation. It is easier to remove steam from dimethyl ether, which can easily be made from even raw methanol by contact at high temperature over an acid catalyst like alumina to form an equilibrium mixture of DME, MeOH and  $H_2O$ . The then unconverted methanol and most of the water present in the equilibrium mixture can easily be separated from the DME and the removed methanol, after some water removal, recycled back to the DME conversion reactor. Use of the DME as the alkoxy feed for hydrocarbon production reduces the amount of water generated in the MTO reaction to only 0.5 mole water per mole of alkoxy equivalent, as against 1.3 for a methanol stream containing 30% of this methanol molar content as water (i.e., a methanol stream containing about 14.4 wt%  $H_2O$ ).

With the process of this invention the operation of each MTO reactor in the series at the same inlet and outlet temperatures and at about the same partial pressure of steam at the outlet without significant changes of pressure therebetween becomes possible (i.e., allowing only for the pressure drop across each reactor needed for gas flow) -- thus providing for uniformity of product distribution production in each of the reactors. For example, with reference to use of dry (0 wt%  $H_2O$ ) methanol as the fresh alkoxy feed for each MTO stage of a five reactor series, wherein the quantity of methanol feed doubles with each succeeding stage, when dry methanol is used as the first stage feed the partial pressure of water in the product gases of the early MTO stages is significantly lower than that of the later MTO stages. Hence, wherein the last MTO stage is operated at an outlet pressure that provides for a partial pressure of water of 2 ata, the first MTO stage operates at an outlet pressure that provides a partial pressure of water of about 30% of that of the last stage. However, by adding water (steam) to the dry methanol feed to the first stage, and/or as needed or desired in the fresh methanol feed to later MTO stages, it is possible to operate each MTO reactor at substantially the same partial pressure of water at its outlet without significantly reducing the pressure at which the last MTO reactor must operate to yield a desired steam partial pressure. It is also possible, as desired, to operate a succeeding reactor at a condition of an inlet-outlet temperature or a pressure that significantly differs from



the operating conditions of preceding reactors without exceeding a partial pressure of steam therein that would prematurely age or destroy its MTO catalyst content -- to permit the control of final product distribution.

Whatever may be the precise nature of the alkoxy feed, typically it will be available for use at about 100°F following its production and cooling to condense excess water from it. Although an MTO catalyst is active for production of hydrocarbon products with respect to any alkoxy compound -- i.e., alkanols, alkylethers, and combinations thereof -- and the process of this invention is applicable to the use of any suitable alkoxy compound, the alkoxy compound preferred for use is methanol, dimethylether, or equilibrium mixtures thereof produced by the catalytic dehydration of methanol. Hereafter, the process of this invention is described with respect to methoxy compounds -- i.e., methanol (MeOH), dimethylether (DME), and mixtures thereof (MeOH + DME). Further, reference to the amount of hydrocarbon products of which the methoxy compound is capable of production is referred to by its "methoxy equivalent." For example, in lb-mole quantities as the point of reference, in the production of olefins by a MTO reaction,



Hence, each mole of MeOH presents one methoxy equivalent and each mole of DME presents two methoxy equivalents. A typical composition of the "gas products" is given in the Examples section of this disclosure.

Within the context of this invention the methoxy compound employed as feed may be methanol only, dimethyl ether only, or mixtures thereof together with such water vapor content as is normal to their production or, preferably, after water that is condensable at about 100°F has been separated therefrom. The nature of the methoxy composition selected as fresh feed to an MTO reactor affects the nature and/or quantity of diluent gas with which it must be combined for proper moderation of the temperature rise and water concentration control within the MTO reactor. On a methoxy equivalent basis, in the production of olefins, each mole of MeOH releases a greater quantity of heat (10,596.7 BTU/lb-mole) and H<sub>2</sub>O by-product than does DME 4,196.7 BTU/lb-mole. Further, since the specific heat of MeOH and DME differ, the composition of the methoxy feed selected influences the degree to which the methoxy + recycle diluent gas composition must be preheated before its admixture with the product effluent gas from a preceding MTO reactor to yield a combined gas stream of suitable temperature and specific heat content for feeding to a succeeding MTG reactor.

An ideal case for purposes of achieving the greatest economics in the overall heat exchange requirements for the MTO hydrocarbon production process is that of exclusive use of DME as the methoxy compound. Next in order of preference is that of the use of a dehydration equilibrium mixture of MeOH + DME as the methoxy feed.

5 A variety of compositions have been disclosed as suitable catalysts for the conversion of methoxy compounds to olefinic hydrocarbons compounds, as for instance in U.S. Patent Nos. 3,702,886; 3,709,979; 3,832,449; 3,998,889; 4,076,842; 4,016,245 and 4,046,859, the disclosures of which are herein incorporated by reference. The above patents particularly discuss the use of these catalyst compositions for a MTG reaction. However, by appropriate control of the  
10 concentration of water over these catalyst compositions during their contact with a methoxy compound, they may be used to promote the MTO reaction without carrying the reaction out to the extent of producing a significant content of saturated and aromatic hydrocarbon products. Further, this invention is applicable to any catalyst composition now existing or which may be developed which catalyzes the conversion of alkoxy compounds to hydrocarbon products,  
15 especially wherein the catalyst composition exhibits a similar sensitivity to temperature and water concentration in terms of its activity and aging characteristics as now existing MTG catalyst compositions do. Examples of such other catalyst compositions include SAPO-34, a silicoaluminophosphate catalyst as described in the presentation papers by Jeffery Lewis et al. and Vara et al. as previously identified, as catalysts that are more selective for olefin production  
20 from methoxy compounds.

It is known, with respect to molecular sieves, like those based on alumina-silica combinations (like ZSM-5, the catalyst used in the methanol to gasoline plant in New Zealand), that a variation in the alumina-silica ratio will affect the acidity of the catalyst. This is for instance discussed in an article by N. Y. Chen and W.E. Garwood in Catalytic Review, Science and  
25 Engineering, Vol. 28, p. 185 (1986). Further, in line with their Bronsted-Lowry acidity character, the acidity of the catalyst varies greatly with steam partial pressure and temperature. This last point stresses the importance of control of these two variables. Finally, introducing other elements into the molecular sieve can affect the acidity strongly, as demonstrated by the introduction of phosphorous by Union Carbide, which led to the SAPO catalyst series, of which  
30 SAPO-34 has been proposed by Union Carbide and UOP for the conversion of methanol to olefins. It is expected that any catalyst with the correct Bronsted-Lowry acidity will convert methanol to ethylene and other olefins. The process of this application is aimed at using such catalysts for operation in a fixed bed. The following discussion is based on the known properties

of SAPO-34, but the process is not limited to use of that catalyst only.

Whatever MTO catalyst composition is selected for use, for essentially complete conversion of the methoxy compound to hydrocarbon to occur, the methoxy containing feed gas must first be conditioned to have about at least a minimum inlet temperature ( $T_i$ ) of about 600 to 700°F, depending upon the nature of the catalyst used, and preferably about 700°F. Further, the feed gas should have a specific heat content that limits the temperature increase ( $\Delta T_R$ ) between the inlet temperature ( $T_i$ ) and outlet temperature ( $T_R$ ) of the MTO reactor preferably to less than 100°F, and more preferably to 75°F or less. The inlet gas temperature may range from about 600 to 725°F to insure complete conversion, while the outlet temperature should be limited to a range of from about 650-800°F. To prevent premature aging or damage of the MTO catalyst a temperature of 800°F should not be exceeded. Also, the partial pressure of steam in the product gases at the reactor outlet should be limited to a range of steam partial pressure of 0.5 to 3.0 ata, preferably 1.5 to 2.8 ata, and most preferably 1.8 to 2.4 ata.

Within the broad ranges of inlet and outlet temperature, various narrower ranges are preferred for purposes of product composition and distribution. To further insure against premature catalyst aging or destruction a temperature of 785°F and partial pressure of steam of 2.2 ata at the reactor outlet is preferably not exceeded.

As before noted, with respect to an MTO reaction it is important to control exposure of the MTO catalyst to both temperature and water (steam) concentration. In operation with a series of MTO reactors, that partial pressure of steam which is the level desired to be realized in the product gases from the outlet of the last MTO reactor in major part determines the pressure at which the earlier MTO reactors in the series may operate. Each earlier MTO reactor will operate at a greater total pressure than that of the last MTO reactor by at least that amount which corresponds to the pressure drop across the inlet to outlet of each intervening reactor. To minimize such pressure drops one may employ reactors of a radial flow design. Consequently, wherein the composition of the methoxy-recycle feed is the same for each reactor in the series, the partial pressure of steam in the outlet product gas from the first reactor will be substantially less than that of the outlet product gas from the last reactor. To even this out, a quantity of steam can be added to the methoxy-recycle feed gas going to the first reactor, which will cause a slight lowering of the pressure at which the last MTO reactor may be operated while still maintaining in the outlet product gas from it the same level desired for steam partial pressure, and at the pressure at which the first reactor operates the partial pressure of steam in its outlet product gas will be similar to that of the last reactor.

The improved process is based on adiabatic reaction in a multiple reactor system with intermediate injection of colder methoxy feed gas. While the different reactors can easily operate under different conditions, it is easier to explain the new process and its advantages by discussing the special case of all reactor steps operating under similar conditions as to the temperature zone for the contact with the MTO catalyst and substantially the same final steam vapor pressure of the reactants in each reactor.

As a typical set of conditions by which to illustrate practice of the process of this invention, unless otherwise indicated, for each reactor in the series a gas stream inlet temperature of 710°F is used and the gas composition for feed thereto is chosen to provide for a  $\Delta T_R$  of 75°F for an outlet gas of 785°F at an outlet pressure that provides for a partial pressure of steam of approximately 2 ata. The methoxy feed for each is MeOH, DME, or a mixture thereof as indicated and is as available for use at a temperature of 100°F. The diluent recycle gas is a portion of the gaseous hydrocarbon product of the MTO process. Further, average specific heat values of the various components of the involved gas streams are utilized for calculations of the specific heat contents of these gas streams, as given in the Examples section of the text which follows. The precise numerical values of these specific heat values vary somewhat in actual practice with variations in the precise compositions of the components and/or the temperature and pressures to which they are actually subjected, as will be appreciated by those skilled in the art. The average specific heat values here used is the average value over the temperature range of 100-800°F. As desired, in putting this invention into actual practice, one skilled in the art may without undue experimentation determine more precise and accurate numerical values for the circumstances of the actual application. As desired, one of ordinary skill may more precisely calculate heatup and cool-down duties as the sums of the incremental heatups or cool-downs from one temperature to another temperature by using the specific values for the specific heat of each compound in the interval between the two temperatures in question. But here, to simplify the discussion, average values of the specific heat of a compound in the temperature region of interest are used. In the discussion of results of the use of this invention, this does not significantly affect the general conclusions discussed about the results and benefits to be had from a practice of this invention.

The composition of fresh methoxy feed to be added to a product effluent gas from a preceding MTO reaction to form a combined gas to be fed to a succeeding MTO reaction may be conceptually viewed as comprising two components which in sum equal the fresh methoxy feed composition. The first component of the fresh methoxy feed is that amount of methoxy

compound that is required to heat up the product effluent gas composition by the delta ( $\Delta$ ) between  $T_R$  and  $T_1$  ( $\Delta T_R$ ) desired to be achieved in the succeeding MTO reaction. The second methoxy component is that quantity of alkoxy plus recycle diluent composition (which diluent composition may contain any desired quantity of steam) which by itself would react with a  $\Delta T_R$  desired for the succeeding MTO reaction (hereafter this component is referred to as the " $\Delta T_R$  balanced alkoxy-recycle diluent composition"). When summed, the first and second methoxy components provide for a total fresh methoxy feed composition having a total specific heat content that will cool down the product effluent gas by heating up the fresh methoxy feed composition to form a combined gas stream of the temperature desired as the inlet temperature ( $T_1$ ) for admission to the succeeding MTO reaction. This in turn then dictates the temperature to which the fresh methoxy feed composition must itself be preheated ( $T_p$ ) before being mixed with the product effluent gas from a preceding reaction zone which is at its reaction temperature ( $T_R$ ) to form the combined gas at temperature  $T_1$  that upon reaction in a succeeding MTO zone will increase in temperature by  $\Delta T_R$  to yield a new effluent gas of an out-let temperature as desired,  $T_R$ .

Wherein one has two gas streams, each being at the same temperature, say  $T_R$ , then upon mixture of one with the other a combined gas stream of the same temperature  $T_R$  is obtained. However, if one takes one gas stream that has already reacted its alkoxy content to reach a temperature of  $T_R$  (the product effluent gas from a preceding zone) and another gas stream which is at a temperature  $T_p$  from which by reaction of its alkoxy content would reach a temperature of  $T_R$  (the fresh methoxy feed gas) and mix the hot with the cooler gas stream, a combined gas stream is obtained having a temperature  $T_1$  which is less than the  $T_R$  of the hot gas stream but greater than  $T_p$  of the cooler gas stream. Thereafter the reaction of the alkoxy content of this combined gas stream will elevate its temperature to  $T_R$ ; this because each of the component parts of this combined gas stream -- the hot and the cooler gas streams -- were either once at the temperature  $T_R$  or by reaction of its alkoxy content would be elevated to the temperature  $T_R$ .

The temperature  $T_1$  that is obtained upon mixing of the two gas streams is related to the specific heat content of each, which in turn is related to the composition and quantity of each. Each molecular species comprising either gas stream has a specific heat value in terms of the heat (BTU) required to elevate its temperature ( $^{\circ}\text{F}$ ) per a unit quantity (lb-mole) of that species. Herein, specific heat values are given in terms of BTU/ $^{\circ}\text{F}$ /lb-mole, meaning the number of BTUs required to elevate one lb-mole of that material by one  $^{\circ}\text{F}$ . The specific heat content of a gas

stream is then the number of BTUs required to elevate that gas stream by one °F, and this specific heat content is the sum of the specific heat value of a species times its quantity for each species contained in the gas stream.

Thus, for example, for a MTO reaction using methanol (heat of reaction to olefins,  $Q_R = 10,596.7$  BTU/lb-mole) to condition the methanol for reaction to olefin products such that the temperature increase due to its reaction is 75°F ( $\Delta T_R$ ) requires that the specific heat content of the feed gas containing this one lb-mole of methanol be  $10,596.7/75 = 141.29$  BTU/°F. Using as an average specific heat value for methanol over the temperature range 635-785°F that of 16.94 BTU/°F/lb-mole the one lb-mole of methanol itself contributes 16.94 BTU/°F of this specific heat content, leaving 124.35 BTU/°F of this content to be satisfied by other components, namely the diluent recycle gas comprising  $C_2$ ,  $C_3$ , steam, or mixtures thereof. With a diluent gas having a composition identical to that of the product olefinic hydrocarbon gas containing 1 mole%  $H_2O$ , assuming in this temperature range that this recycle mixture has an average specific heat value of 21.64 BTU/°F/lb-mole then 5.746 lb-moles of this gas would be required for each 1 lb-mole of methanol to form a feed gas that would react with a temperature increase of 75°F. This  $\Delta T_R = 75^\circ F$  balanced gas composition would then be:

$CH_3OH = 1.00$  lb-mole,

Recycle product gas = 5.746 lb-mole,

Specific Heat Content = 141.29 BTU/°F.

This feed, as first preheated to 710°F, when contacted with an MTO catalyst will react to form a product gas having a temperature of 785° and a specific heat content which, for discussion purposes, is assumed to be the same as the feed gas from which it was formed, namely 141.29 BTU/°F.

The hot product gas at 785°F has a content of heat in excess of that at which it would otherwise have a temperature of 710°F of 10,596.7 BTU, which is the heat released by reaction of the methanol from which the olefin product gas stream was formed. Transfer of this 10,596.7 BTU of heat from this product gas stream to another medium will reduce the temperature of this product gas stream from its 785°F temperature to a temperature of 710°F. The medium of transfer can be a cooler gas stream, and the transfer can be accomplished by indirect exchange as through the heat transfer surfaces of an adiabatic heat exchanger or by direct gas-to-gas contact by admixture of the two gases.

In this invention the transfer of the excess heat of the product gas to the cooler feed gases is in part accomplished through adiabatic heat exchangers -- to preheat a fresh feed gas charges

to a temperature  $T_p$  -- and in part by direct gas-to-gas contact -- to finally warm up the preheated fresh feed gas charge from its  $T_p$  preheat temperature to a temperature  $T_i$  desired for contacting it with a MTO catalyst. The direct gas-to-gas heat exchange is accomplished in the intermediate reactors in the series, and the product gas from the last of the MTO reactions in series is used for indirect heat exchange through adiabatic heat exchangers to warm up the fresh feed gases to their preheat  $T_p$  temperature.

As to the direct gas-to-gas heat exchange to warm up a fresh feed gas from its preheat temperature  $T_p$  to the  $T_i$  temperature desired for its contact with an MTO catalyst, the specific heat content of the fresh feed gas governs how much it can be warmed up by the cooling down from  $T_R$  of the hot product gas with which it is mixed. The amount by which the fresh feed gas will be warmed up ( $T_i - T_p$ ), while the product gas is cooled down ( $T_R - T_i$ ) is related to the ratio of the specific heat content of the fresh feed gas ( $S_f$ ) to the specific heat content of the product gas ( $S_p$ ) according to the equation:

$$S_f \frac{(T_R - T_i)}{(T_i - T_p)} = S_p.$$

For the case under discussion, wherein it is desired to have the next reaction begin at a temperature of  $T_i = 710^\circ\text{F}$ , the composition and quantity of the new feed gas are governed then by

$$S_f (710 - T_p) = 10,596.7$$

and its specific heat content is a function of the temperature to which it is preheated before admixture with the hot product gas. Selecting then, for discussion purposes, a feed gas preheat temperature of  $635^\circ\text{F}$  ( $T_p$ ), the specific heat content of the fresh feed must equal that of the product gas with which it is to be mixed, and the combined gas stream will have a specific heat content that is the sum of its component parts. To then have this combined gas stream react to a new product gas temperature  $T_R = 785^\circ\text{F}$  requires that it contain a quantity of alkoxy compound, here for discussion purposes, methanol, to heat its now doubled specific heat content of  $282.58 \text{ BTU}/^\circ\text{F}$  by  $75^\circ\text{F}$ , or  $282.58 \times 75 = 21,193.5 \text{ BTU}$ . This quantity of heat is supplied through the reaction of 2 lb-moles of methanol ( $Q_R = 10,596.7 \text{ BTU/lb-mole}$ ) which contributes 33.88  $\text{BTU}/^\circ\text{F}$  towards the needed 141.29  $\text{BTU}/^\circ\text{F}$  specific heat content required for the new feed gas, leaving 107.41  $\text{BTU}/^\circ\text{F}$  of the heat content to be supplied by diluent gas. Where this remaining quantity is supplied by a diluent gas comprising recycle of a portion of the olefin product gas, then 4.963 lb-moles of such recycle gas is required. Hence the composition of the

fresh feed gas would be:

$$\text{CH}_3\text{OH} = 2.00 \text{ lb-mole,}$$

$$\text{Recycle product gas} = 4.963 \text{ lb-mole,}$$

$$\text{Specific Heat Content} = 141.29 \text{ BTU/}^\circ\text{F}$$

- 5 Reaction of the combined gas mixture will then produce a new product gas having a temperature of 785°F and a specific heat content of 282.58 BTU/°F.

This new product gas ( $T_R = 785^\circ\text{F}$ ;  $S_P = 282.58 \text{ BTU/}^\circ\text{F}$ ) may be used as the hot gas source for mixture with a new portion of fresh methoxy feed gas to form a combined gas mixture for another reaction over an MTO catalyst between any reaction temperature zone of  $T_1$  to  $T_R$  as may  
10 be desired.

Take for instance that for this next reaction it is desired to contact the next MTO catalyst at a temperature  $T_1 = 700^\circ\text{F}$  and have a new product gas temperature from that reaction limited to 740°F. In this case the previous product gas requires cool down from 785°F to 700°F for a  $T_R - T_1$  of 85°F, meaning the previous product gas must give up  $282.58 \text{ BTU/}^\circ\text{F} \times 85^\circ\text{F} = 24,019$   
15 BTU of heat which is then available for warm up of the new methoxy feed gas to the desired inlet temperature of 700°F. Once this previous product gas component has been cooled to 700°F, at its specific heat content of 282.58 BTU/°F, to increase its temperature to the  $T_R = 740^\circ\text{F}$  desired for the new product gas requires  $282.58 \text{ BTU/}^\circ\text{F} \times 40^\circ\text{F} = 11,303 \text{ BTU}$  of heat to be released by reaction of methanol contained in the new feed charge. To this end, after reaction by methanol  
20 has warmed itself or its reaction product up by 40°F to consume  $16.94 \times 40 = 677.6 \text{ BTU}$  of the heat of its reaction, there remains  $10,596.7 - 677.6 = 9,919.9 \text{ BTUs}$  of heat to warm up the previous product gas, thus  $11,303/9,919.9 = 1.1395 \text{ lb-mole}$  methanol are required to reheat the previous product gas from 700 to 740°F. If again the new feed gas has been preheated to a  $T_P$  temperature of 635°F the composition and quantity of the new feed gas is governed by

$$25 \quad S_F (700 - 635) = 24,019$$

or its  $S_F$  required is 369.523 BTU/°F of which 19.303 BTU/°F is provided by the methanol required to reheat the previous product gas that will become part of the combined gas stream to be reacted. Hence, 350.22 BTU/°F of value remains to be filled in the new feed gas by methanol and recycle constituents and these constituents must react from a  $T_1$  temperature of 700°F to the  
30 new temperature desired of 740°F. Here, to moderate the reaction of one lb-mole methanol to a 40°F increase in temperature upon its reaction requires a specific heat content of  $10,596.7/40 = 264.91 \text{ BTU/}^\circ\text{F}$ , of which that one-lb-mole of methanol contributes 16.94 BTU/°F, leaving 247.98 BTU/°F of content to be supplied by a recycle diluent gas. Again, using dewatered olefin



product gas as the recycle gas diluent would require 11.459 lb-mole of such diluent. Hence, the  $\Delta T_R = 40^\circ\text{F}$  balanced gas composition would be:

$$\text{CH}_3\text{OH} = 1.00 \text{ lb-mole,}$$

$$\text{Recycle} = 11.459 \text{ lb-mole}$$

$$\text{Specific Heat} = 264.92 \text{ BTU/}^\circ\text{F.}$$

To supply the 350.22 BTU/°F needed, 1.322 times this quantity of the  $\Delta T_R = 40^\circ\text{F}$  balanced gas composition is needed. Hence the new feed gas would be:

	Component To Reheat Previous Product Gas	$\Delta T_R = 40^\circ\text{F}$ Balanced Composition x 1.322	New Feed Gas
CH <sub>3</sub> OH	1.1395	1.322	2.4615
Recycle	-0-	15.149	15.149
Specific Heat Content	19.303	350.22	369.523

It should be clear from the general discussion given above that in order for the new process to effect significant savings in heat exchange the above mentioned  $T_p$  temperature of the added feed should be significantly lower than the  $T_i$  temperature of inlet to the reactor obtained after addition of the hot exit gas from the earlier reactor. The given examples clearly demonstrate that a reduction of about a factor of 2 can be obtained with as little as  $60^\circ\text{F}$  difference between these two temperatures. It is, however, preferred to use a more optimal temperature difference of about  $200^\circ\text{F}$  and a larger number of reactors, like 10, preferably 5 to 8, so that a more sizeable heat exchange duty reduction of about one order of magnitude can be obtained, especially when using DME only.

It should be understood that especially when using a larger number of reactors, the pressure drop per reactor as a sum may begin to exert a negative effect on the size of the heat exchanger. This has been taken into account in calculation of the advantages to be obtained.

Accordingly, to maximize the efficiency of heat exchange operations (which is a variable of pressure, the  $\Delta T$  of heat exchange and the volume of gas treated for heat exchange) while also maximizing the saving required for fresh feed preheating and/or product gas cool-down for product recovery the following conditions are preferred:

- (1) preheating of the fresh feed gas to a temperature within  $75$  to  $260^\circ\text{F}$  of the  $T_i$  temperature selected for admission of the combined gas stream to the succeeding MTO reaction zone, preferably to within  $100$  to  $210^\circ\text{F}$ ;

- (2) formation of the combined gas stream to have a temperature  $T_1$  from 650-720°F, and preferably from about 675-720°F;
- (3) selection of the alkoxy content of the fresh feed stream to have a heat of reaction content that, upon reaction of that alkoxy content thereof, would increase the temperature of the combined gas stream by a  $\Delta T_R$  of 30-120°F, more preferably by 50-100°F and most preferably by 50-85°F; and
- (4) formation from reaction of the combined gas stream in the succeeding MTO reaction zone of a new effluent gas having a temperature  $T_R$  of from about 700 to 800°F, preferably from about 730 to 800°F, and more preferably of from about 750 to 785°F.

Figure 1 illustrates one embodiment of the process which employs five MTO reactors in series flow, reactors 10, 20, 30, 40 and 50. A methoxy feed with an appropriate amount of water to allow initiation of reaction over the MTO catalyst together with an appropriate amount of recycle diluent gas at 100°F, is fed by line 2 to heat exchange 3 and is there preheated to  $T_p$  (i.e., 710°F) then fed by line 4 to the inlet of reactor 10 and passed into contact with an MTO catalyst. The product effluent gas is passed by line 11 to line 12. A fresh quantity of methoxy feed at  $T_o$  (i.e., 100°F) passes from line 5 through heat exchanger 6 and is preheated to a temperature  $T_p$  and then passed by line 7 through metering valve 7a into admixture with the product effluent gas in line 12. A further quantity of recycle diluent gas 5a at  $T_o$  (i.e., 100°F) passes through heat exchanger 8 and is preheated to temperature  $T_p$ , then passed by line 9 through metering valve 9a into admixture with the product effluent gas and methoxy feed in line 12. The combined gas stream passes from line 12 into contact with the MTO catalyst in reactor 20 and the product effluent gases pass therefrom by line 13 into line 14 where the product effluent gas becomes admixed with a further quantity of methoxy feed and recycle diluent gas, each at temperature  $T_p$ , as metered into line 14 through valves 7b and 9b respectively. Again, the product effluent gas from reactor 30 passes by line 15 into a further quantity of methoxy and recycle gases each at  $T_p$ , as metered in through valves 7c and 9c respectively, and the combined gases pass by line 16 into contact with an MTO catalyst in reactor 40. The product effluent gas from reactor 40 passes by line 17 into mixture with a further quantity of methoxy and recycle diluent gas at  $T_p$ , as metered in through valves 7d and 9d respectively and the combined gases pass by line 18 into contact with an MTG catalyst in reactor 50. The product effluent gas from reactor 50 passes by line 19 to subsequent processing units where it is cooled to 100°F for separation and recovery of its various components, such as its olefinic hydrocarbon content in part for recycle use as a diluent gas and

in part to be processed into its various fractions, particularly to separately recover its ethylene content and its propylene content.

In the process of converting an alkoxy compound to olefinic products by contact with an MTO catalyst it is necessary to heat up feedstocks of alkoxy-diluent gases from their unit available temperature ( $T_O$ ) to a temperature at which they will react over an MTO catalyst, namely  $T_1$ . By reason of the exothermic reaction of the alkoxy compound to olefinic products the product effluent gas resulting from contact with an MTO catalyst has an even higher temperature,  $T_R$ . In order to condition the reaction gases for recovery of their olefin products, it is necessary to cool the product effluent gas from its temperature  $T_R$  to a temperature at which its water content condenses, typically about 100°F.

Typically, the product gases at  $T_R$  and feedstock gases at  $T_O$  are passed through adiabatic heat exchangers wherein heat content  $Q$  is exchanged between the product gases and feedstock gases through a heat exchange surface that separates these gas streams, whereby the product gases cool down in temperature to the extent they transfer a content  $Q$  of their heat to the feedstock gases which are thereby increased in temperature.

In an ideal case, the product gas contains a quantity of heat  $Q$  that is in excess of that quantity required to heat up the feedstock gases to  $T_P$  by an amount that is equal to the heat released by the alkoxy compound that reacted to form the product gases. Thus, following the first heat exchange between the product gases at  $T_R$  and feedstock gases at  $T_O$  through the heat exchange surface of an adiabatic heat exchanger, the feedstock gases are heated up to  $T_P$  and the reaction gases are cooled down to a temperature  $T_x = T_R - (T_P - T_O)$ . Hence, to recover water from the reaction gases it is necessary to cool them further from their  $T_x$  temperature to about 100°F, which is typically the temperature  $T_O$  at which the feedstock gases are available since a major portion of the feedstock gases are hydrocarbons, recovered after separation of water from the reaction gases, and used as the recycle or diluent component of a feedstock. In this last step of reaction gas cooling, the reaction gases at  $T_x$  are heat exchanged in an adiabatic heat exchanger operating with chill water, typically at a chill water temperature of 70°F.

With the process of this invention it is possible to realize significant economies in the heat exchange requirements in terms of the combined size of the heat exchangers required for feedstock heatup duties and the heat exchangers required for the final step of reaction gas cool-down for separation of water and other condensible liquid components from the olefin gas product.

For purposes of influencing the hydrocarbon distribution of the product in favorable ways,

it is possible with the process of this invention to tailor the conditions of inlet-outlet temperature and effluent gas steam partial pressure of water for any reactor in the series to a set of conditions different than other reactors in the series. Operations at lower partial pressures of steam over the MTO catalyst, such as from about 0.5 to 1.5 ata, may favor a higher product of ethylene compared to other olefins.

For the composition of the recycle diluent gas a number of possibilities exist, which each have some advantage.

The easiest in operation is to recycle part of the total product stream, only after cooling down and separation of condensed water. Apart from the ease of this mode of recycle operation, it has the drawback that part of the recycle is ethylene product, which is endangered by repeated contact with the MTO catalyst. This danger exists also for the propylene in the recycle, but possibly to a lesser degree.

This leads to the first improvement that of recycling only the  $C_{3+}$  fraction of the product stream. As it is most likely that in the workup of the product stream a  $C_2$ - $C_{3+}$  separation will be the first step in handling the dried and compressed product gas stream, this will make the recycle somewhat more expensive in nature. But, most likely, any substantial yield improvement in ethylene will more than compensate for this extra cost. Another factor resulting from the higher molecular weight of the  $C_{3+}$  species as the recycle composition is that it makes the heat exchange more difficult. However, as the proposed process has already significantly reduced the total heat exchange to very manageable levels, a partial increase to this heat exchange may be quite acceptable.

It is easier to recycle any  $C_{4+}$  material that can be condensed at reasonable pressure rather easily out of the dried gas product stream. One could even add a  $C_{3+}$  stream to the feed and use this recycling  $C_{3+}$  stream (together with small make-up amounts) as the heat absorbing recycle diluent gas. Such a  $C_{3+}$  stream has a still higher molecular weight and its extra cost has to be determined. Again, the ease of applying such a higher molecular weight stream has its definite advantages.

It is expected that the use of any of these higher molecular weight recycle systems will improve the fixed bed operation even more than a total dry product recycle. It is expected, that a total dry product recycle or a  $C_{3+}$  recycle will for all practical purposes eliminate the formation of coke and other by-products generated by the local overheating of regenerated catalyst particles that occurs in a fluidized bed of MTO catalysts. Further, practice of this invention with a fixed bed of MTO catalyst is expected to improve the ethylene to propylene ratio of the product

compared to that obtained in a fluidized bed. Higher molecular weight recycle streams will improve this ratio further. As ethylene is under general circumstances a more valuable product than propylene, an increase in the ethylene to propylene ratio is very desirable.

In another embodiment of the invention the heat exchange duties required for conversion of alkoxyl compound to olefins may be even further reduced by operating the first MTO reactor in a mode wherein a portion of its produce effluent gas is recycled back to its inlet for combination with fresh alkoxy-diluent recycle feedstock admitted thereto.

This mode is illustrated in Figure 2, wherein feed gas preheated to a temperature  $T_p$  is routed by line 70 to the inlet 72 of MTO reactor 74. Product gas at a temperature  $T_R$  is taken from reactor 74 by line 76 and is then split into two product streams, one of which proceeds through line 80 to the next MTO reactor in the series (not shown) and the other product gas portion is routed by line 78 to a hot gas fan 82 wherein it is recompressed to a pressure equal to that of the feed gas to MTO reactor 74 and then routed by line 84 for addition to reactor inlet 72 in admixture with feed gas routed to the inlet 72 via line 70. In this mode, as illustrated by Figure 2, the alkoxy-diluent recycle feedstock would be preheated to a preheat temperature  $T_p$  and upon combination with the recycle portion of the product stream at  $T_R$  would form a combined gas stream of temperature  $T_i$  for contact with the MTO catalyst. In this mode of operation the composition of the alkoxy-diluent recycle feedstock is adjusted to provide an amount of alkoxy compound relative to the diluent recycle content of this feed that upon reaction to olefin product provides a heat of reaction that raises the temperature of the combined gas stream from  $T_i$  to  $T_R$ . Otherwise stated, the quantity of alkoxy compound relative to the diluent recycle content of the feed is that which by heat of reaction would increase the temperature of the feed alone from its preheat temperature  $T_p$  to  $T_R$ .

This product recycle mode of operation for the first MTO reactor means that preheating of the feedstock gases can more efficiently be accomplished, i.e., a smaller heat exchange area is required, because the differential heat exchange temperature  $\Delta T$  as reflected in the heat exchange factor ( $1/\Delta T$ ) is now  $T_R - T_p$  rather than  $T_R - T_i$ . To accomplish this product recycle requires a slight recompression of this portion of the product gas from its reactor outlet pressure ( $P_o$ ) to the gas pressure required for the reactor inlet ( $P_i$ ), in other words, to compensate for the pressure drop occurring across this reactor. This may readily be accommodated with a hot fan, a conventional item of equipment. However to utilize a conventional hot fan for this recompression, the volume of product recycle that can be accomplished is limited by the fan capacity and this in turn will generally set the preference for the conditions to be employed in the

subsequent MTO reactors in the series. That is, for a given total of olefin production desired, once the capacity of the first reactor product recycle is determined by the fan capacity, the most optimum of conditions for subsequent feed preheat temperature and the number of MTO reactors may be selected for the balance of the desired total hydrocarbon production. As may be appreciated, wherein one is content to produce only that quantity of hydrocarbon product that a single reactor operating on a hot fan recycle could itself produce, then the process of this invention can be practiced with a single MTO reactor.

The following examples illustrate operations in accordance with the process of the invention and, in some cases, for comparison purposes illustrate operations in accordance with prior art practice. Unless otherwise indicated the following values were applied in preparation of the examples.

- (1) Dimethylether (DME) - 0.88 gaseous products + 0.94 H<sub>2</sub>O ( 8,393.4 BTU/lb-mole DME)
- (2) Methanol (MeOH) - 0.44 gaseous products + 0.97 H<sub>2</sub>O (10,596.7 BTU/lb-mole MeOH)

The composition of the gaseous product resulting from 100 lb-moles of MeOH or DME is, for purposes of these examples, assumed as follows:

	<u>Product Component</u>	<u>Moles /100 MeOH</u>	<u>Moles/100 DME</u>	
	<u>Olefins</u>			
	Ethylene (C <sub>2</sub> H <sub>4</sub> )	25	50	
	Propylene (C <sub>3</sub> H <sub>6</sub> )	10	20	
20	Butenes (C <sub>4</sub> H <sub>8</sub> )	2	4	
	<u>Saturated Hydrocarbon By-Products</u>			
	Methane (CH <sub>4</sub> )	1	2	
	Ethane (C <sub>2</sub> H <sub>6</sub> )	1	2	
	Propane (C <sub>3</sub> H <sub>8</sub> )	1	2	
25	Butanes (C <sub>4</sub> H <sub>10</sub> )	1	2	
	<u>Gaseous By-Products</u>			
	Hydrogen (H <sub>2</sub> )	1	2	
	Carbon Monoxide (CO)	1	2	C a r b o n
	Dioxide (CO <sub>2</sub> )	1	2	
30	<u>Water Reaction By-Product</u>	97	94	

While this as a product composition for a MTO process is reported by the J. Lewis et al. presentation paper previously identified, in actual practice of this invention one may expect considerably less production of by-products, meaning that a higher yield of olefins may be expected.

To determine heatup and cool-down duties for the feed and product gas streams involved,

average specific heat values were used for the compounds and compositions of interest determined for two temperature ranges, namely the 100-725°F range relating to feed gas preheating and the 725-800°F range wherein the reaction of preheated feed gases to olefinic product gases occurs. The average specific heat values used are as follows:

	Average Specific Heat	Temp. Range 100-725°F; BTU/°F/lb-mole	Temp Range 725-800°F; BTU/°F/lb-mole
5			
	(1) DME	19.979	25.76
	(2) MeOH	14.1888	17.32
10	(3) H <sub>2</sub> O	8.3984	8.88
	(4) Dry Olefinic Product	17.321	21.575
	(5) Olefinic Product with 1 mole% H <sub>2</sub> O Content ("wet")	17.232	21.448
15	(6) C <sub>3</sub> , Dry	24.354	30.730
	(7) C <sub>3</sub> , "Wet"	24.195	30.512
	(8) C <sub>4</sub> , Dry	31.930	40.103
	(9) C <sub>4</sub> , "Wet"	31.695	39.791
20	(10) C <sub>5</sub> (Pentane) Dry	42.051	53.360
	(11) C <sub>5</sub> , "Wet"	41.715	52.915

Operations in accordance with the proposed invention in comparison to that for a single reactor pass method of converting the same quantity of methoxy equivalent is discussed below. In each of Example 1 to 5, unless otherwise indicated, the effluent gas temperature at the outlet  
 25 (T<sub>R</sub>) of each MTO reactor is 800°F, the inlet gas temperature (T<sub>I</sub>) of the gas feeds to each MTO reactor is 725°F, and the partial pressure of steam in the effluent gas of each MTO reactor is 2.0 ata. A pressure drop of 0.20 ata across each MTO reactor is assumed. Example 1 is a comparative example and illustrates the conversion of the methoxy component of the feed gas by a single pass through one reactor. Examples 2 to 5 illustrate the conversion of a similar  
 30 quantity of methoxy component in a series of five MTO reactors operating in accordance with the process of this invention. The relative heat exchange surface area (A<sub>R</sub>) required for feed gas

warm-up in the examples is calculated according to the relationship:

$$A_R = Q (1/\Delta T)(1/P)^{0.6}$$

wherein Q is the quantity of heat required to warm-up a feed gas from temperature  $T_O$  to  $T_P$ , with  $T_O = 100^\circ\text{F}$  for all examples; the  $\Delta T$  is  $T_R - T_P$  with  $T_R = 800^\circ\text{F}$  for all examples; and P is the pressure of the last reactor effluent gas and is that pressure in atmospheres absolute (ata) that provides for a partial pressure of steam in the effluent gas of 2.0 ata. Quantities are given in moles per hour (MPH) for lb-moles of the components indicated. The quantity of methoxy equivalent processes is that amount which are on an annual operating basis would produce 5,000,000 metric tons per year (MTPDY) of ethylene product.

#### 10 Example 1 (Comparative):

This example illustrates a single pass MTO conversion of methoxy compound, analogous to that of the single pass process MTG scheme employed in New Zealand. Three situations are presented: (a) wherein the methoxy component is methanol and water in a 1 to 0.25 mole ratio, (b) wherein the methoxy component is an equilibrium mixture (equilibrium constant  $K = 4.45$ ) made from the methanol-water composition above, and contains methanol, dimethyl ether and water, and (c) wherein the methoxy component is relatively dry dimethyl ether (i.e., DME:H<sub>2</sub>O is 10:1). The recycle diluent gas for each situation comprises a "wet" recycle of product gases wherein the product gases recycled at  $100^\circ\text{F}$  have a content of water of 1 mole %. In each situation the feed gas is preheated to  $725^\circ\text{F}$  in an adiabatic heat exchanger wherein the hot product gas is used as the hot heat exchange fluid.

Feed MPH	(a) MeOH + 0.25H <sub>2</sub> O	(b) Equilibrium Mix MeOH + DME	(c) DME + 0.1 H <sub>2</sub> O
MeOH	19,018.5	4440.8	—
DME	—	7,288.8	9,509.25
H <sub>2</sub> O	4,754.6	12,043.4	950.9
25 "Wet Recycle" - i.e., Product Gas w/1mole % H <sub>2</sub> O	107,958.3	51,207.9	43,513.4
Ar	4,197,359	3,107,868	1,693,216
Final P. (ata)	11.5	7.0	10.9



**Example 2**

A total methoxy equivalent of 19,018.5 MPH is processed in accordance with the invention in a series of five MTO reactors. For the first MTG reactor of the series a portion of this methoxy equivalent content as methanol, together with an appropriate amount of "wet" recycle product gas and a quantity of water to provide for a reactor outlet steam pressure of 2.0 ata at a total pressure of 0.8 ata higher than the final pressure of Reactor V outlet is preheated to 725°F, the remainder of this methoxy equivalent content as relatively dry DME (i.e., DME:H<sub>2</sub>O=10:1) is combined with the "wet" recycle product gas and preheated to the T<sub>p</sub> temperature indicated and proportioned as fresh methoxy feed to the four subsequent MTO reactors wherein each portion is combined with the effluent gas from a preceding MTO reactor before being fed to its succeeding MTO reactor. A pressure drop of 0.2 ata across each reactor is assumed. The relative heat exchanger surface areas required for preheating the feed to the first reactor, Reactor I, and for preheating the feeds for the subsequent four reactors, Reactors II-V, are given below, as is the total of the relative heat exchange surface area required.

T <sub>p</sub> : Temperature (°F) Fresh Feed Preheat for Reactors II-V	Final Product Gas Pressure, (ata) of Reactor V	Steam Partial Pressure Range of Reactor II-V (ata)	A <sub>R1</sub> : Relative Heat Exchange Surface Area, Reactor I	A <sub>R II-V</sub> : Relative Heat Exchange Surface Area, Reactors II-V	A <sub>R</sub> Totals: Total Relative Heat Exchange Surface Area	A <sub>R</sub> Total Per 100 MeO Equiv- alents
650	6.30	1.997-2.067	89,649	549,964	639,613	3,363
600	5.08	1.966-2.046	166,020	411,199	577,219	3,035
550	4.37	1.946-2.037	193,540	231,124	424,665	2,233
500	3.87	1.915-2.025	234,117	156,380	398,497	2,053

The above data demonstrates that as the fresh feed gas preheat temperature T<sub>p</sub> is lowered, that the contribution of the heat exchange duty requirements for preheating the first reactor feed gas to the total heat exchange duties becomes greater. As a consequence, even though of the total methoxy converted that which is converted in the first reactor is a small fraction, the requirements for its warm-up together with its recycle gas content is of major influence on the total heat exchange area necessary.

**Example 3:**

In a manner like that of Example 2, a total methoxy equivalent of 19,018.5 MPH is processed wherein the feed methoxy to the first reactor is DME having a quantity of H<sub>2</sub>O to provide for a reactor outlet steam pressure of 2.0 ata at a total pressure at the outlet of Reactor I which is 0.8 ata greater than the outlet pressure of Reactor V. The feed for Reactor I is

preheated from 100°F to 725°F in an adiabatic heat exchanger. For the subsequent reactors dimethyl ether having a molar ratio  $\text{DME:H}_2\text{O} = 10:1$  is used as the methoxy component of the feed. These subsequent feeds are preheated from 100°F to a temperature  $T_p$  as indicated below. The following results are given:

5	$T_p$ Temperature (°F) Fresh Feed Preheat for Reactors II-V	Final Product Gas Pressure, (ata) of Reactor V	Steam Partial Pressure Range of Reactors II-V (ata)	$A_{R1}$ Relative Heat Exchange Surface Area, Reactor I	$A_{R\text{II-V}}$ Relative Heat Exchange Surface Area, Reactors II-V	$A_R$ Totals: Total Relative Heat Exchange Surface Area	$A_R$ Total Per 100 MeO Equivalents
10	650	6.44	2.00-2.098	87,160	543,012	630,175	3,313
	600	5.05	1.955-2.041	141,958	345,581	487,548	2,564
	550	4.37	1.946-2.037	184,359	226,476	410,835	2,160
15	500	3.88	1.898-2.018	221,127	152,745	374,016	1,967

#### Example 4:

The same methoxy feed composition as in Example 3 is utilized under similar conditions except that the first MTO reactor is now operated in a mode wherein the inlet feed thereto is preheated to 675°F and outlet product gas temperature is 725°F for a  $\Delta T_R$  therein of 50°F. In the subsequent reactors the new DME + recycle feed is preheated to 500°F and after admixture with hot product gas from the preceding reactor reaches an inlet temperature of 675°F and reacts to an outlet temperature of 725°F.

25	$T_p$ Reactor Feed Preheat Temp., (°F)	Final Product Gas Pressure (ata) of Reactor V	Steam Partial Pressure of Reactor v Outlet	$A_{R1}$ Relative Heat Exchange Surface Area, Reactor I	$A_{R\text{II-V}}$ Relative Heat Exchange Surface Area, Reactors II-V	$A_{R\text{TOTAL}}$ Total Relative Heat Exchange Surface Area I-V	$A_R$ Total Per 100 MeO Equivalent
	I @ 675°F	---	---	92,314	---	433,055	2,277
30	II-IV @ 675°F	4.65	1.907	---	340,741		

Although the process of this invention has been described with reference to its preferred embodiment, from this description those skilled in the art may appreciate changes and modifications that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

## CLAIMS:

1. A method of making olefinic compounds by contacting an alkoxy compound with an MTO catalyst, comprising the steps of:

combining an effluent gas product from a preceding MTO reaction zone which is at a  
5 temperature  $T_R$  with

- (a) an alkoxy compound; and
- (b) a diluent gas comprising a  $C_2$  recycle gas, a  $C_3$  recycle gas, steam, or mixtures thereof,

to form a combined gas stream wherein in the combined gas stream;

- 10 1. the alkoxy compound is present in a quantity that provides an alkoxy equivalent which exceeds that added to the preceding MTO reaction zone from which the effluent product gas was formed; and
- 2. the diluent gas composition is of a temperature and composition and is present in an amount that:
  - 15 (a) provides for the combined gas stream to have a temperature of from about 600°F to about 725°F, and
  - (b) provides for the combined gas stream to have specific heat content that limits temperature increase of the gas stream to less than 150°F upon reaction of the alkoxy compound content thereof to  
20 olefinic compounds;
  - (c) provides for a total water content following reaction of the alkoxy compound to olefinic compounds that does not exceed a partial pressure of water (as steam) of 3.0 ata; and

contacting the combined gas stream with a fixed bed of MTO catalyst in a succeeding  
25 reaction zone to form a new effluent product gas.

2. The method of claim 1, wherein the combined gas stream has a temperature of from about 700 to about 725°F, and the temperature increase of the gas stream on contact with the MTO catalyst is less than 100°F.

3. The method of claim 2, wherein the alkoxy compound is DME and the diluent gas  
30 comprises a portion of the final effluent product gas after water removal therefrom.

4. The method of claim 1, wherein from three to ten MTO fixed bed reaction zones are arranged in series flow and the combined gas stream comprising the effluent gas product from a preceding MTO reaction zone and the alkoxy compound and diluent gas is at a temperature of from about 650 to about 725°F when first contacted with an MTO catalyst in a succeeding MTO reaction zone and has a specific heat content that provides for a temperature of effluent gas exiting the succeeding zone of from about 700 to about 800°F.

5. The method of claim 4, wherein with respect to each MTO reaction zone each combined gas stream enters each zone at substantially the same inlet temperature and each effluent gas exits each zone at substantially the same outlet temperature.

6. The process of claim 5, wherein the partial pressure of water in an effluent gas does not exceed 2.2 ata.

7. The method of claim 1, wherein the alkoxy compound and diluent gas are preheated to a temperature of from about 400 to about 600°F prior to being combined with the effluent gas product from a preceding MTG reaction zone.

8. The method of claim 7, wherein the combined gas stream has a temperature of from about 650 to 725°F and the temperature increase of the gas stream is about 75°F or less.

9. The method of claim 8, wherein the alkoxy compound is DME and the diluent gas comprises a C<sub>2</sub> recycle gas and a C<sub>3+</sub> recycle gas in a molar ratio of C<sub>2</sub>:C<sub>3+</sub> of from about 3:1 to about 1:3.

10. The method of claim 1, wherein a series of MTO reactors is employed and the combined gas stream supplied to the last MTO reactor of the series has a temperature of from about 625 to 700°F and a specific heat content that limits the new effluent product gas temperature to 760°F or less.

11. The method of claim 10, wherein the combined gas stream supplied to the MTO reactors other than the last MTO reactor of the series has a temperature of 650 to 700°F and a specific heat content that limits its temperature increase to a range of 70 to 90°F.

12. The method of claim 1, wherein a series of MTO reactors is employed and a portion of the effluent product gas from the first MTO reactor is recycled back to the first MTO reactor inlet to become admixed with feedgas to the first MTO reactor to form a combined gas stream feed to the first MTO reactor having a temperature of from about 600 to 725°F and a specific heat content that limits temperature increase of the gas stream to less than 150°F.

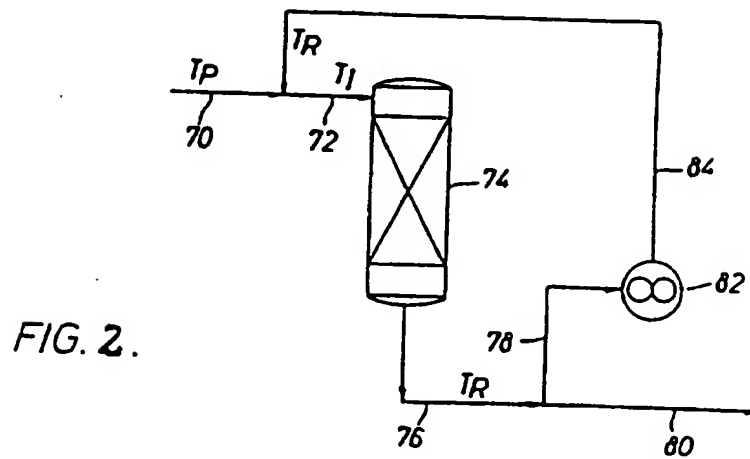
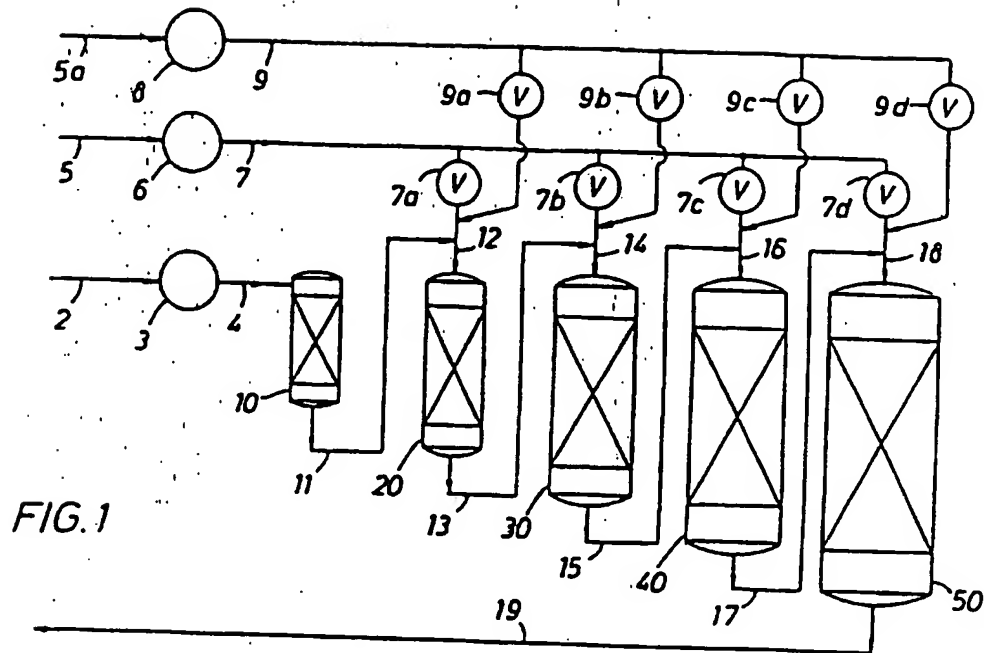
13. The method of claim 12, wherein the combined gas stream feed to the first MTO reactor has a temperature of from about 650 to about 720°F and a specific heat content that limits temperature increase of the gas stream to 100°F or less.

14. The method of claim 1, wherein the diluent gas contains steam in an amount sufficient to provide for a partial pressure of steam in the new effluent product gas of from about 1.8 to about 2.4 ata.

15. The method of claim 1, wherein a series of MTO reactors is employed, and of that total quantity of alkoxy compound converted to hydrocarbon compounds, no more than 20% of the total alkoxy compound is converted in the first MTO reactor of the series.

16. The method of claim 1, wherein each effluent gas product has a partial pressure of water of from 1.85 to 2.2 ata.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/05266

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C07C 1/00, 2/00, 4/00, 5/00, 6/00

US CL :585/312, 313, 315, 324, 638, 639, 640

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/312, 313, 315, 324, 638, 639, 640

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, Y	US 5,602,289 A (VAN DIJK) 11 February 1997, col. 28, line 30 through col.30, line 35.	1-16
Y	US 4,654,453 A (TABAK) 31 March 1987, col. 2, lines 5-10	1-16

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	
*A* document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*E* earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*O* documents referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	*A* document member of the same patent family

Date of the actual completion of the international search

15 MAY 1997

Date of mailing of the international search report

24 JUN 1997

 Name and mailing address of the ISA/US  
 Commissioner of Patents and Trademarks  
 Box PCT  
 Washington, D.C. 20231

Facsimile No. (703) 305-3599

Authorized officer

GLENN CALDAROLA

Telephone No. (703) 305-6118